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EFFECT OF SURFACE ON CATHODE POLARIZATION DURING THE ELECTRODEPOSITION OF COPPER[1]

BY W. GAUVIN[2] AND C. A. WINKLER[3]

Abstract

Measurements in a modified Haring cell have shown that at current densities above approximately 0.6 amp. per dm.^{2}, definite values of the cathode polarization are attained during the electrodeposition of copper from acid copper sulphate solutions, providing sufficient time is allowed for the cathode surface to attain a steady state corresponding to the conditions of electrolysis. At lower current densities, the base metal structure is perpetuated in the deposit, and the cathode polarization will depend upon the surface condition of the electrode initially. The results account for the lack of agreement in polarization values obtained by different workers using the Haring cell, and indicate that crystal size is fundamentally related to true current density, rather than to cathode polarization. A method is outlined for obtaining reproducible cathode-polarization–current-density curves, substantially corresponding to steady state values.

The use of addition agents during the electrodeposition of metals has been standard commercial practice for many years. Such agents include substances of widely different chemical constitution and behaviour, but they have in common, when present in comparatively minute amounts in an electrolytic bath, the ability to impart acceptable characteristics to a metallic deposit which, in their absence, might be considered unsatisfactory. It is necessary to control the concentration of addition agents within comparatively narrow limits, since optimum improvement of the deposit cannot be realized with too little of the agent, while an excess generally results in an unsatisfactory condition of the deposit and an excessive loss of power through increased polarization. Control of the effective concentration of addition agents is difficult, however, mainly because of the small concentration generally used. Chemical control of phenol as an addition agent in electrotyping solutions is possible (10), but such an analysis takes no cognizance of anodic oxidation and cathodic reduction and gives, therefore, only approximate results.

Estimation of the concentration of addition agent by measurement of the cathode polarization in a special electrolytic cell that bears his name has been suggested by Haring (9). The cell consists simply of a relatively long, narrow box, one end of which is covered with the anode, the other with the

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cathode. Two intermediate electrodes of copper gauze are so situated between the anode and cathode as to divide the cell into three equal compartments. The potential drop across the cathode compartment, less the *IR* drop across the same thickness of solution, measured as the potential drop across the middle compartment, gives the cathode polarization. True values of the polarization are obtained only if the intermediate electrodes are not polarized, and if the lengths of all compartments are accurately the same for constant cross-section of the cell throughout its length.

By this method, close control of the concentration of glue used as addition agent in copper and lead refining was asserted to be possible, but the results obtained with this cell by other workers show very poor agreement (5, 6, 8, 9, 12, 15, 17, 18). Since there appears to be no reason for doubting the fundamental soundness of the Haring method, the lack of agreement between different investigators presumably arises from inadequate attention to the variables that might influence the measurements. An investigation was undertaken, therefore, to determine the conditions under which reproducible cathode polarization measurements might be made with the Haring cell, and to assess accurately its applicability to the problem of determining addition agent concentration during copper electrodeposition. The present paper is limited to discussing the development of a method whereby satisfactory reproducibility may be obtained with the cell; its use for determining addition agent concentration will be dealt with in a later paper.

Experimental

The electrolytic cell used in the present studies was a slightly modified form of the Haring cell, and is depicted in Fig. 1, which is virtually self-explanatory. Briefly, it consisted of two blocks of cast copper, used as anode and cathode, inserted between bakelite walls and bottom. All parts were machined with precision, so that thin paper gaskets, lightly coated with paraffin, were sufficient to make the cell water-tight. Two intermediate electrodes of 20-mesh copper gauze, with a coat of electrodeposited copper, were inserted in grooves made in the bakelite walls; they divided the cell into three equal compartments. These intermediate electrodes were held firmly in place and connected to the electrical circuit by copper clamps screwed to the two binding posts on the sides of the cell.

A 6-volt battery, with recharging circuit, constituted the current source. Potential differences between electrodes were measured with a type K Leeds and Northrup potentiometer, with the usual apparatus to complete the circuit. Currents from 250 ma. to 1.5 amp. were measured with a calibrated ammeter that could be read to 1 ma., while currents of less than 250 ma. were measured with a milliammeter with an error not greater than 0.1 ma.

The cell was carefully levelled to position in a thermostat controlled to within 0.05° C. All metallic parts of the cell were prevented from coming into contact with the thermostat liquid by means of a coating of high-melting paraffin. Since bakelite is a poor heat conductor, sufficient time was allowed

to permit the cell to come to the thermostat temperature. During this time, the solution to be investigated, contained in a flask immersed in the thermostat liquid, was also permitted to come to the bath temperature.

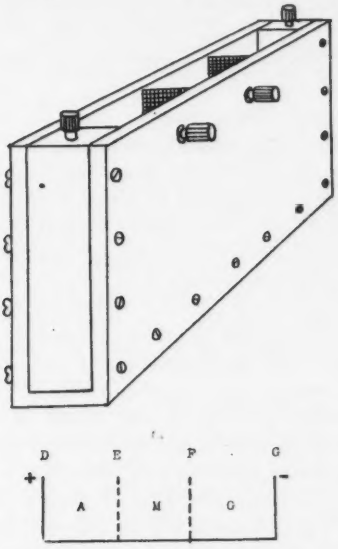

FIG. 1. *The Haring cell.*

Materials:
Walls and bottom: bakelite, $\frac{1}{4}$ in. thick.
Electrodes: solid cast copper, $\frac{21}{32}$ in. thick.
Intermediate electrodes: copper gauze, 20-mesh.

Dimensions:
Height of electrodes: 8.6 cm.
Width of electrodes: 2.6 cm.
Inside length of cell: 15 cm.
Immersed area of electrodes: 10 cm.^{2}

Prior to mounting in the cell, new electrodes were treated in one of two ways: (*a*) Polished successively with No. 2, 1, 0, and 00 emery papers, following the procedure used in the preparation of a metallic sample for micrographic inspection, without, however, the final "wheel" treatments (in which could be used, for example, tripoli, alumina, and tin oxide as the polishing materials). The polished electrodes were then washed thoroughly in benzene, and rinsed in distilled water, after which they were etched in a solution containing 435 ml. per litre of concentrated sulphuric acid and 72 ml. per litre of concentrated nitric acid. (*b*) If unpolished electrodes were to be used in an experiment, they were immersed for 15 min. in a boiling solution of sodium hydroxide (15 gm. per litre), sodium carbonate (60 gm. per litre), and sodium cyanide (7.5 gm. per litre). Thorough rinsing with distilled water followed either the acid etch or the alkaline cleaning treatment.

Since all potential measurements were made on a relative basis, it was not necessary to know exactly the apparent electrode area covered by the

solution, but it was essential that the area covered should be reproducible in successive experiments. Solutions were therefore measured into the cell with a volumetric flask, calibrated to deliver sufficient solution to cover 10 sq. cm. of the electrode faces, as determined by measurement with a vernier caliper. Care was taken to have the solution wet the electrodes uniformly to the prescribed height, indicated by a mark on the bakelite walls, close to the electrodes.

Correction was made from time to time for slight inequalities in the distances between the four electrodes in the cell. These inequalities, even if not present initially, are introduced to an appreciable extent as deposition of metal on the cathode and solution of metal from the anode take place with prolonged use of the cell. Mechanical measurement of the interelectrode distance was not found sufficiently accurate, and an alternative method was used, based on the observation that in an unacidified copper sulphate solution containing 125 gm. per litre of $CuSO_4 \cdot 5\,H_2O$, the anode and cathode polarizations were found not to exceed 12 mv. for apparent current densities of 0.3 to 1.0 amp. per dm.^{2} The determination of the correction is most readily understood by reference to the diagram of Fig. 1. For a constant current I, the potential differences between D and E, and D and F are first measured, D being in both cases connected to the positive side of the source of current. Since the fall of potential between two electrodes is equal to the sum of the anode and cathode polarizations and the IR drop through the solution between them, the drop between D and E will be the sum of A_A (the anode polarization), IR_A (the drop through the solution in compartment A), and A_C (the cathode polarization) or:

$$\text{Fall in potential between } D \text{ and } E = A_A + IR_A + A_C \qquad (1)$$

Similarly, between points D and F, if the cathode polarization is designated by M_C, and the drop through the additional compartment by IR_M:

$$\text{Fall in potential between } D \text{ and } F = A_A + IR_A + IR_M + M_C \qquad (2)$$

M_C and A_C, the values of the cathode polarization at the two intermediate electrodes, are the same, because the same current I is used in both cases, and the two electrodes consist of the same material and have the same structure (essentially copper deposited under the same conditions), hence the value of IR_M will be obtained directly by subtracting Equation (1) from (2).

If the same current I is then applied between E and F (E being connected to the positive side), and the anode polarization is designated by M_A and the cathode polarization by M_C, then:

$$\text{Fall in potential between } E \text{ and } F = M_A + IR_M + M_C \qquad (3)$$

M_A and A_A will not be exactly the same, because, although the same current I is used, M_A represents the anode polarization at a gauze electrode, and A_A, that at a solid electrode of slightly different area, but since neither exceeds 12 mv., their difference will be small compared with the values of the IR drops in the various compartments which, at the current density used in these

experiments (0.8 amp. per dm.^{2}), were of the order of 1300 mv. This fact was further shown by reversing the polarity during the measurements, the new values agreeing within 3 to 4 mv. with the previous ones. Hence the value of IR_A is given quite accurately by subtracting Equation (3) from (2). The value of IR_C for the third compartment of the cell may be evaluated in exactly the same way. Since the cross-section of the cell is constant, the relative lengths of the three compartments are then calculated directly from the relative values of R_A, R_M, and R_C.

Results and Discussion

Preliminary experiments were made, using polished electrodes in a solution containing 125 gm. of reagent grade copper sulphate and 50 gm. of concentrated sulphuric acid per litre. For future reference, this solution may be designated as the standard electrolyte (solution No. 17). Measurements of the cathode polarization were not reproducible, variations as large as 100% being noted even when the procedures outlined by other users of the Haring cell were closely followed. A study of the change of cathode polarization with time was therefore made.

With the standard electrolyte and electrode surfaces polished as described previously, it was found that the cathode polarization decreased during the first 30 to 90 min. of the electrolysis. Typical curves, obtained at 24.8° C. and an apparent current density of 2 amp. per dm.^{2} are shown in Fig. 2. The initial values for a given current density at a given temperature were quite

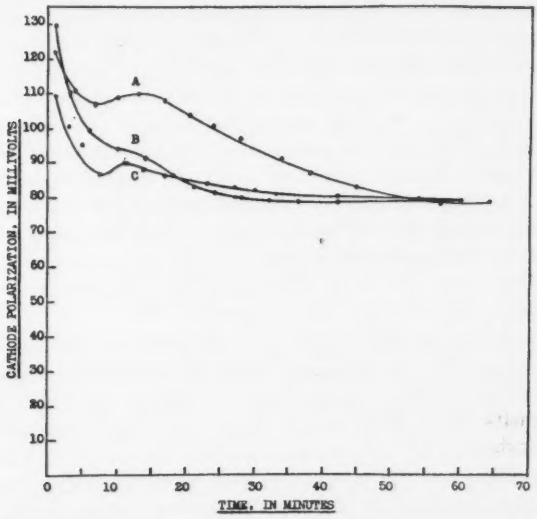

FIG. 2. *Change of cathode polarization with time on polished surfaces. Solution: No. 17. Apparent current density: 2 amp. per dm.^{2} Temperature: 24.8° C. Initial surface: polished base metal.*

variable, but the final values were essentially the same, 75.2 to 80.5 mv. In every case, an initial rapid decrease of the polarization from the original value occurred. This was followed, almost without exception, by a slight increase, generally after 10 to 12 min. after which the polarization decreased gradually to the final value. The general course of the curve, representing the rate at which the final value was attained, varied with different electrode specimens under otherwise comparable conditions.

The change in cathode polarization with time might be ascribed to slow attainment of steady state conditions in the electrolyte, particularly in the film in contact with the cathode. It has been demonstrated (4), however, that in nickel deposition from "still" solutions, a constant cathode film thickness and a constant concentration gradient across the film are fully established about two minutes after the start of the electrolysis. Since the current was maintained rigorously constant throughout the experiments, and constancy of current, of cathode film thickness, and of concentration gradient in the diffusion layer imply constant rates of migration, convection, and diffusion, it seems very unlikely that the time factor involved in these studies is attributable to establishment of steady state conditions in the electrolyte. There remains the possibility that the electrode surface must attain a condition characteristic of deposition under given experimental conditions before a steady state in the over-all electrodeposition process can be completely established.

Numerous studies of hydrogen overvoltage, particularly the work of Bowden and Rideal (3), have shown that the amount of hydrogen that must be deposited on the cathode to raise its potential 100 mv. is not a specific property of the metal atom, but depends only on the physical structure of the surface. Bowden and Rideal showed that this amount was very small for a mercury surface and much greater for a freshly etched silver surface of fine crystalline structure. Ageing of the latter somewhat reduced the amount of hydrogen needed, while polishing the same silver surface considerably reduced it. From these and numerous other observations, it was concluded that the accessible area of a mercury surface was considerably smaller than that of a silver one, the latter being reduced by polishing. Moreover, Foerster quotes some results showing that polishing increases the hydrogen overvoltage on cadmium (7); from this it can be inferred that polishing decreases the true area of the metal surface.

The changes in cathode polarization with time, depicted in Fig. 2, may be explained reasonably by assuming that deposition on a polished surface brings about an increase in true surface area of the electrode. The true current density then would be decreased for a constant current, and the cathode polarization correspondingly reduced, in accordance with the observed behaviour. Moreover, the lack of reproducibility in initial polarization values, and differences in shape of the curves between the initial and final values, are readily accounted for by failure to reproduce accurately, by polishing methods, the same surface characteristics for different electrode specimens.

This, in turn, may be ascribed to the formation of a hardened skin—the Beilby layer—on the surface of the cathode during the process of polishing, which may or may not be completely removed by a subsequent etching. Portevin and Cymboliste (13) have made a thorough micrographic study of the effect of polishing on the structure of the deposit subsequently obtained on the polished surface, and showed that very small cavities, cracks, and irregularities may be caused by polishing, which may cause considerable variation in the crystalline structure of the deposit.

On the other hand, final attainment of a surface of definite characteristics, representing a steady state condition corresponding to conditions prevailing in the electrolytic bath, would account for the definite value of the cathode polarization eventually obtained. Support for these views was obtained from

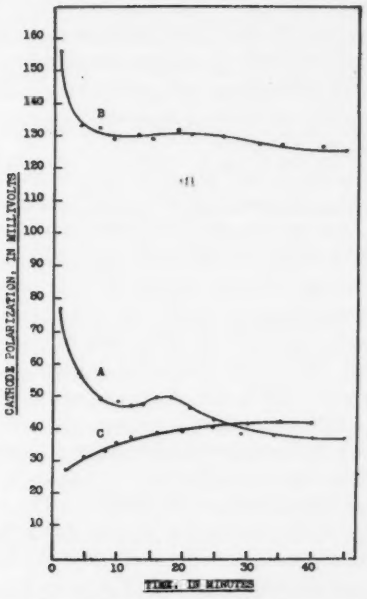

FIG. 3. *Effect of change in current density on surfaces.*

Solution: No. 17.
Apparent current density:
For A: 0.875 amp. per dm.²
B: 3.3 amp. per dm.²
C: 0.875 amp. per dm.²
Temperature: 25° C.
Initial surface:
For A: polished base metal.
B: that at the end of A.
C: that at the end of B.

an experiment, using standard electrolyte (solution No. 17) at 25° C., the results of which are shown in Fig. 3. Curve *A* was obtained with a polished surface and an apparent current density of 0.875 amp. per dm.² Such a relatively low apparent current density is conducive, as has been frequently

reported, to formation of a comparatively coarse crystalline deposit. When the steady state polarization was attained, the current was switched off for 10 min. after which electrolysis was resumed at an apparent current density of 3.3 amp. per dm.^{2} The lapse of 10 min. before resumption of electrolysis should have been ample to allow complete dissipation of the cathode film created at the lower current density, since Brenner showed (4) that the film was completely dissipated three minutes after interruption of the current. Electrolysis at an apparent current density of 3.3 amp. per dm.^{2} gave results shown by Curve *B*. The higher current density promotes rapid nuclear formation, hence a finer crystalline deposit (14, 19), with accompanying increase in true cathode surface. The steady state polarization value is therefore less than the initial value on the coarse surface. Following a second interruption of 10 min., electrolysis was again resumed at the original current density of 0.875 amp. per dm.^{2} The results, shown in Curve *C*, gave an initial cathode polarization lower than that corresponding to the steady state value for this current density, as might be expected because of the finer crystalline structure of the surface, with its greater true area. As electrolysis proceeded, however, the cathode polarization increased to essentially the same steady state value as before.

Further confirmation that the cathode polarization should attain with time a definite steady state value under given conditions of electrolysis was sought by using cathodes having widely different initial surface characteristics, instead of the closely similar polished surfaces previously used. One cathode was given a very coarsely crystalline surface by deposition from the standard electrolyte at an apparent current density of 0.6 amp. per dm.^{2} and temperature of 26.4° C. The electrolyte was then renewed, and electrolysis continued at a current density of 2 amp. per dm.^{2} The cathode-polarization–time curve is shown in Fig. 4, Curve *A*. A second cathode was given a comparatively fine-grained surface structure by deposition from standard electrolyte at an apparent density of 2 amp. per dm.^{2} and temperature of 2.0° C. Electrolysis was then continued in renewed electrolyte at an apparent current density of 2 amp. per dm.^{2} and temperature of 26.4° C. The corresponding cathode-polarization–time curve is also shown in Fig. 4, Curve *B*. The changes in polarization with time can again be accounted for by an increase of true cathode area as a finer deposit is laid down (Curve *A*), and a decrease in true area as a more coarsely crystalline surface is produced (Curve *B*). The final values of the cathode polarization (72 and 76.4 mv.) agree within the error of the experiment, and are, moreover, essentially the same as the steady state values found previously for closely similar conditions of electrolysis when polished electrodes were used (75 to 80 mv.).

It is a logical corollary of the behaviour with cathodes of different initial surface characteristics, that no change in cathode polarization should be observed when the true electrode area is not allowed to change, providing other conditions of electrolysis remain the same. To investigate this point, the final value of the cathode polarization was established at 26.4° C. in

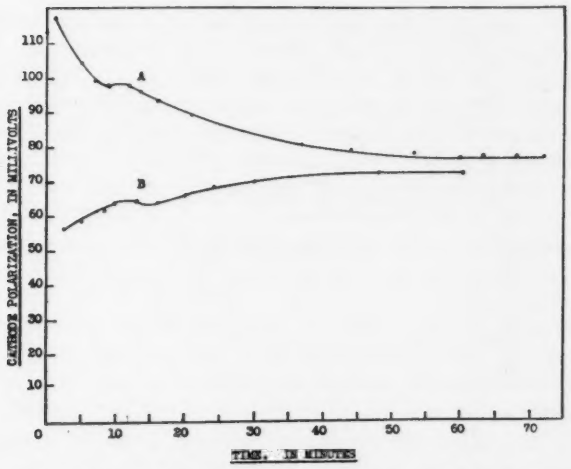

FIG. 4. *Attainment of equilibrium polarization on different surfaces.*

Solution: No. 17. Temperature: 26.4° C. Apparent current density: 2 amp. per dm.²
Initial surface:
For A: that obtained from the same solution, under the same conditions, but at an apparent current density of 0.6 amp. per dm.²
For B: that obtained from solution No. 17, at an apparent current density of 2 amp. per dm.² and a temperature of 2° C.

standard electrolyte at an apparent current density of 2 amp. per dm.² on a polished electrode (Fig. 5, Curve *A*). Without otherwise disturbing the system, the current was then switched off for 10 min. after which electrolysis was resumed at the same current density. The result is shown in Fig. 5, Curve *B*. This curve was reproduced almost exactly with longer periods of interruption of the current. Obviously, the initial and final values of the polarization remain the same in Curve *B*, but it is interesting to note that after 10 to 12 min. a slight increase in polarization, similar to that noted previously, was observed when electrolysis was resumed after each interruption of the current.

Following upon these experiments, the electrolyte was removed, the cell thoroughly rinsed with distilled water, and dried. After 48 hr., electrolysis was resumed under the same conditions as before, but the cathode polarization values obtained at the beginning of this experiment showed a marked increase over the previous steady state value. As electrolysis was continued, however, the polarization diminished as shown in Curve *C*, Fig. 5, eventually attaining within 3 mv. of the steady state value. The change in surface conditions of the electrode was ascribed, at first, to "ageing," as observed with the silver electrode by Bowden and Rideal (3). The cell was therefore emptied, and again rinsed thoroughly with distilled water, and dried. After one-half hour, electrolysis was resumed, with the results shown in Curve *D*, Fig. 5. Appar-

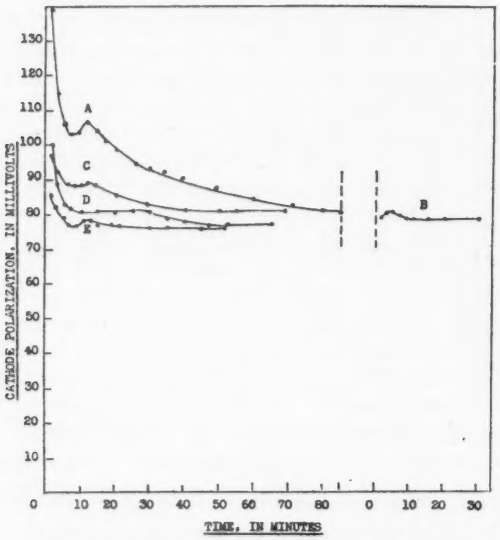

FIG. 5. *Reproducibility of equilibrium polarization.*

Solution: No. 17. *Temperature: 26.4° C.*
Initial surface:
For A: polished electrode.
B: that at the end of A, and 10 min. later.
C: that at the end of B, and 48 hr. later.
D: that at the end of C, and 30 min. later.
E: that at the end of D, after acid etching.
Apparent current density: 2 amp. per dm.²

ently the change in surface conditions was not one involving a prolonged "ageing" effect, but even with comparatively short exposure to air some change, presumably oxidation, had occurred to an extent sufficient to alter the surface characteristics of the cathode rather seriously. The cell was then rinsed thoroughly with distilled water at the temperature of the bath before being used again, the electrodes given an "acid dip" for a few seconds, the cell rinsed thoroughly with distilled water as before, and electrolysis resumed immediately upon introducing the electrolyte, which had been kept at the temperature of the thermostat. The results obtained are shown in Curve *E*, Fig. 5. Obviously, the effect of exposing the surface to the atmosphere, though not entirely removed by the few seconds "acid dip," was largely reduced.

While the data so far presented demonstrate, with some assurance, that reproducible steady state values of the cathode polarization could be obtained at an apparent current density of 2 amp. per dm.², it was of special interest for future purposes to determine the time required to attain steady state values at lower current densities, where the surface characteristics of the base metal

may influence the nature of the deposit to a marked degree. Wood (20), in particular, has shown by X-ray studies that at apparent current densities below 1.2 to 1.5 amp. per dm.^{2} the structure of the base metal was "continued" or reproduced in the deposit when the surface was chemically clean. It must be noted here that this critical range of the current density may be altered by different electrolyte compositions. Wood obtained his results with a solution containing 200 gm. per litre of copper sulphate and 100 gm. per litre of sulphuric acid.

The steady state times at different apparent current densities were determined in a series of experiments, before each of which the surface of the cathode was brought to standard conditions by electrolyzing in fresh electrolyte at an apparent density of 2 amp. per dm.^{2} until the usual steady state polarization value was reached. After the standard surface was thus obtained, the cell was in every case emptied, the cathode etched as described before, and fresh electrolyte at the bath temperature introduced into the cell.

In the first experiment, the solution was electrolyzed at a current density of 0.2 amp. per dm.^{2} At this low current density, the polarization assumed a constant value almost immediately after the current was adjusted, and no change was observed during a period of 60 min. After bringing the surface back to standard conditions, as described above, electrolysis was resumed at 0.2 amp. per dm.^{2} for five minutes. The apparent current density was then increased to 0.4 amp. per dm.^{2} and maintained constant at this value, and here again no significant change in polarization occurred after as much as 60 min. of electrolysis. The explanation of the behaviour for both of these experiments would seem to be that electrolysis at these low current densities perpetuates the surface structure of the base metal in the deposit. Hence, reproducible cathode polarization measurements at these low current densities will be possible only if the cathode surface is always the same initially.

In a third experiment, the apparent current density was again increased in steps of 0.2 amp. per dm.^{2} every five minutes, starting at 0.2 amp. per dm.^{2} When the apparent current density was increased to 0.6 amp. per dm.^{2} and maintained constant at this value, the cathode polarization increased slowly with time to a steady state value after approximately 50 min. In the fourth experiment, the same procedure was repeated until an apparent current density of 1.2 amp. per dm.^{2} was reached, at which point the current was maintained constant, and polarization measurements were taken against time, until steady state polarization was obtained. Finally, a fifth curve was determined in exactly the same manner at an apparent current density of 2 amp. per dm.^{2}

The results of these experiments are shown in Fig. 6. The cathode polarization is plotted as a dotted line against the apparent current density to yield a curve for the experimental points representing average polarization values attained after five minutes electrolysis with successive increments of 0.2 amp. per dm.^{2}, starting with an initial current density of 0.2 amp. per dm.^{2} on the "standard base." The agreement for the various cathode polarization values

obtained during these five experiments was in every case better than 2.6 mv. Referring again to Fig. 6, it will be noticed that subsidiary time scales are placed immediately below each curve representing attainment of the steady state polarization. These time scales are adjusted so that the zero points correspond to the lapse of five minutes following adjustment of the current at each current density value.

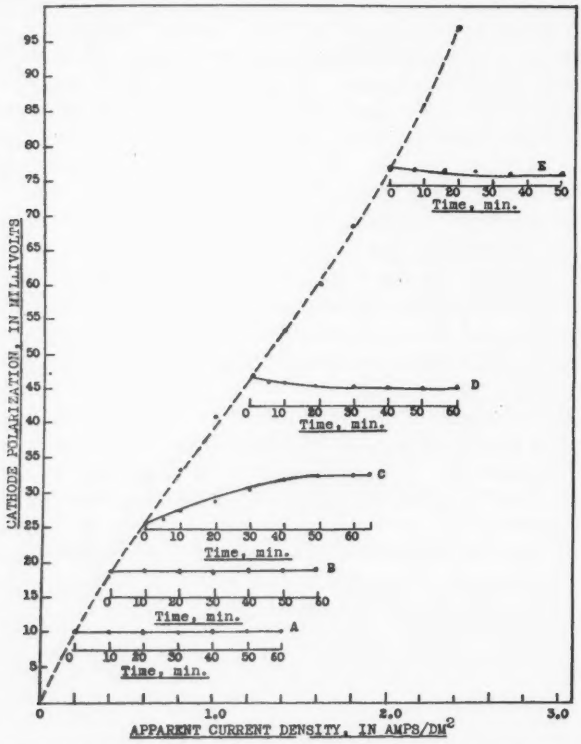

FIG. 6. *Deviation of polarization from equilibrium values. Solution: No. 17. Temperature: 25° C. Initial surface: standard base.*

It is obvious from the figure that at an apparent current density of 0.6 amp. per dm.² the steady state polarization is not attained in less than about 50 min. (Curve *C*), while at 1 amp. per dm.² or higher, the steady state polarization is attained within five minutes of adjusting the current. The influence of the base metal surface at 0.6 amp. per dm.² is still readily discernible. For example, at this current density, the time curve shows an increase in cathode polarization to the steady state value. This corresponds to an increase in true current density, or to a decrease in true cathode surface area, which may be interpreted as a change from a finer to a coarser-grained cathode surface

(compare with Fig. 3, Curve *C*, and Fig. 4, Curve *B*). Bearing in mind that low current densities tend to produce coarsely crystalline deposits, it is evident that deposition at 0.6 amp. per dm.^{2} did not take place on a surface representing steady state conditions at a lower current density, namely, 0.4 amp. per dm.^{2}, but on a surface having the finer-grained structure characteristic of deposition at a higher current density. This evidently corresponds to the initial surface of the cathode, the "standard base" established at an apparent current density of 2 amp. per dm.^{2} the nature of which was perpetuated in the deposits laid down at the lower current densities of 0.2 and 0.4 amp. per dm.^{2}

It is not difficult, on the basis of the results that have been presented, to account for the lack of agreement in cathode polarization values obtained by different workers using the Haring cell. Measurement of the polarization at any given current density, after an arbitrarily determined time, say five minutes following establishment of the current, a method that has been followed frequently in the past, obviously cannot lead to reproducible values, unless the time chosen is at least the minimum required to establish steady state conditions. Moreover, this minimum time will vary with the initial condition of the cathode surface and the current density used.

The slight increase in cathode polarization observed after approximately 10 min. of electrolysis seems to be a general behaviour. On a few occasions, it was not observed, but this might mean simply that it occurred so rapidly that the time intervals between successive measurements were too long to allow it to be detected. No satisfactory explanation of this effect has yet been found. It is possible that it is associated with an oxidation–reduction reaction. A somewhat analogous behaviour has recently been reported (16) and ascribed to the influence of an oxide film, the formation of such film being assumed to be caused by the air present over the solution (1, 11). Obviously, more experimental information is required for a satisfactory explanation, and a further study of this point is contemplated.

The results of the present study are in contradiction to the Blum and Rawdon theory (2), according to which the change from a coarsely crystalline surface to a fine-grained deposit should be associated with an increase in cathode polarization, and vice versa. Curves *B* and *C*, Fig. 3, and the curves of Fig. 4 show exactly the opposite effect. It appears that the logical relation is one between crystal size and true current density, and not between cathode polarization and crystal size.

It seems reasonable to conclude from these experiments that for given electrolytic conditions in a given system, there corresponds a definite steady state value of the cathode polarization, associated with a steady state surface of a definite true area corresponding to the conditions prevailing. Except at very low current densities, any initial cathode surface will gradually attain the steady state surface characteristic of the given conditions.

Since the use of the Haring cell in the control of those addition agents that cause an increase in the cathode polarization involves the determination of

this increase as compared with the polarization determined in a solution free from these agents, it is at once obvious that the prime requisite of the method is reproducibility of the values within a small experimental error. To measure the cathode polarization at any other point than the steady state would be misleading (Fig. 2). As establishment of this steady state surface involves the lapse of anywhere from 50 to 90 min., it might appear that the determination of a complete cathode polarization curve for a wide range of apparent current densities is a lengthy process. However, Fig. 6 shows that the abbreviated method followed in the present study gives reproducible results. Numerous subsequent determinations showed that the cathode polarization curve of Fig. 6 could be reproduced with an experimental error not exceeding 3 mv., provided the same initial surface was used. Clearly, a polished surface, however carefully prepared, cannot be used (Fig. 2). Only a steady state surface obtained under rigorously fixed conditions of electrolysis will answer the purpose and will permit satisfactory reproducibility. Standard bases other than that used here could be used, but the cathode polarization values determined at the lower current densities will differ from those shown in Fig. 6. Effects of this type have been observed and results of a study of them will be published shortly.

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THE HYDRATION OF THE ALUMINATES OF CALCIUM

IV. HYDROTHERMAL REACTIONS OF TRICALCIUM ALUMINATE AND ITS HYDRATES[1]

BY G. M. HARRIS[2], W. G. SCHNEIDER[2], AND T. THORVALDSON[3]

Abstract

A study was made of the hydrothermal reactions of tricalcium aluminate and its hydrates between 120° and 350° C. Homogeneous samples of the hexahydrate of tricalcium aluminate may be prepared by treatment of the aluminate or its hexagonal hydrate in saturated steam at temperatures up to 150° C. At temperatures of 250° C. and above, under conditions favouring rapid hydrolysis, such as the addition of water to the anhydrous aluminate or hydroaluminate before autoclaving and rapid elevation of the temperature of the autoclave, crystals of calcium hydroxide and of a hydroaluminate of lower lime–alumina ratio appear, usually mixed with the isometric hexahydrate. The new hydroaluminate occurs as rectangular, elongated, prismatic plates of low birefringence, refractive index 1.627, and has a lime–alumina ratio probably lower than 1.5. The hexagonal hydrate of tricalcium aluminate gives on hydrothermal treatment a better yield of the low-limed hydroaluminate than does the anhydrous aluminate. Only partial hydrolysis of the hexahydrate was obtained under any of the conditions used, but the hexagonal hydrate, autoclaved for 12 hr. at 350° C., gave products composed almost entirely of the rectangular plate hydroaluminate and calcium hydroxide. No free hydrated alumina was found in the hydrothermal products.

The rectangular plate hydroaluminate of calcium may also be prepared by the action of calcium hydroxide on hydrated alumina in saturated steam at 350° C. It is therefore a stable product under those conditions.

At temperatures below 250° C. birefringent crystalline material is also formed on autoclaving tricalcium aluminate or its hydrates under conditions favouring hydrolysis. The experimental evidence indicates that one of the products is the birefringent calcium hydroaluminate formed on autoclaving the lower calcium aluminates at temperatures of 105 to 150° C. (5).

Precast Portland cement concrete products, when subjected to steam-curing, normally contain an excess of water, and the conditions for the formation of these birefringent hydroaluminates of calcium are therefore present. The same applies to the commercial steam-curing of other materials containing free lime and hydrated alumina. The formation of these hydroaluminates may explain the peculiar effect on the tensile and compressive strength of mortar and concrete test pieces produced by hydrothermal treatment at temperatures above 150° C. (9).

Introduction

It is generally considered that the isometric hexahydrate of tricalcium aluminate is the most stable hydroaluminate of calcium in contact with saturated water vapour at and above room temperature. Under these conditions the hexagonal hydrates of tricalcium aluminate appear to be

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metastable with respect to the hexahydrate, although no transition point has been discovered. According to Lafuma (2) hydrated dicalcium aluminate when heated in contact with its mother liquor at 80° C. changes to this stable product. It is also one of the products of the hydration of Portland cement.

Tricalcium aluminate hexahydrate has been usually prepared in this laboratory (6) by the direct hydration of the pure aluminate in saturated steam at 150° C. Other workers (1, p. 183) have not found this method entirely satisfactory for obtaining a pure product, reporting the presence of an anisotropic impurity. Workers in this laboratory have also observed this, particularly if the anhydrous aluminate contains a slight excess of alumina (in the form of the next aluminate lower in lime), but also at times when pure tricalcium aluminate had been used. The present paper reports a study of the hydrothermal behaviour of tricalcium aluminate and of its hexagonal and isometric hydrates.

Experimental

1. *Experimental Methods and Materials*

The hydrothermal treatments were carried out as follows. The samples, contained in platinum crucibles, were supported above water in air-tight, silver-lined steel tubes heated at 120° C. in an air oven. In some cases this arrangement was used at higher temperatures, the closed tubes being heated in an autoclave containing water. At 150° C. an electrically heated autoclave of hammered copper was used, the platinum crucible containing the aluminate being protected by a brass container perforated near its base. At higher temperatures the crucibles were suspended from the plunger of an electrically heated steel bomb similar to that described by Morey and Ingerson (4). The amount of water used was such that the crucibles were in all cases surrounded by the vapour phase. By means of auxiliary heating, the temperature of the bomb could be raised from room temperature to the maximum in from 5 to 30 min.

The hydrothermal behaviour of the following was studied:

(1) Anhydrous tricalcium aluminate,

(2) The hexagonal hydrate of tricalcium aluminate,

(3) Pure samples of the isometric hexahydrate of tricalcium aluminate.

2. *Preparation of Tricalcium Aluminate and Its Hydrates*

The preparation of anhydrous tricalcium aluminate and of its hexahydrate has been described in previous papers (6, 8).

A series of five preparations of the hexahydrate, starting with the anhydrous aluminate, gave, on five to nine days' treatment in saturated steam at 120° C. with subsequent drying *in vacuo* over lime, products containing from 5.98 to 6.00 moles of water per mole of the aluminate. Seven similar preparations carried out at 150° C. gave, after 7- to 14-day treatments, products containing from 5.98 to 6.01 moles of water. None of these samples showed any birefringent material under the microscope. In no case was there evidence

of any appreciable condensation of water in the protected crucible containing the aluminate.

The hexagonal hydrate of tricalcium aluminate was prepared as follows. The anhydrous tricalcium aluminate was added gradually to distilled water containing pure ice. The heat of hydration was thus absorbed as latent heat of fusion and the temperature of the mixture remained at the freezing point. The mass, contained in a closed gold-lined tube, was kept at this temperature, with frequent shaking, for two or three weeks and then dried at 21° C. in evacuated desiccators over saturated solutions of lead nitrate (98% humidity), potassium acetate (21% humidity), and anhydrous magnesium perchlorate. The observed results varied somewhat with the size of the batch. Stored over lead nitrate, the samples appeared dry in four to six days when the aluminate still held approximately 18 moles of water. This fell to about 14 moles in 6 to 10 days and then decreased very slowly to somewhat over 12 moles in 30 to 40 days. The saturated solution of potassium acetate reduced the water held by the aluminate to somewhat over 10 moles, while magnesium perchlorate reduced it to 7½ moles in 13 days. The last drying agent was found to absorb some moisture from samples already dried to constant weight over calcium oxide. The hydrate appeared to be composed entirely of clusters of hexagonal plates. These observations are in general agreement with previous work (7).

3. *Conditions Favouring the Formation of Anisotropic Material During the Hydration of Tricalcium Aluminate*

Fig. 1 is a typical photomicrograph (crossed Nicols) of material obtained by moistening anhydrous tricalcium aluminate before treating it in the autoclave, raising the temperature in five minutes to 150° C., and keeping it constant for four days. The product apparently held six moles of water after drying over lime, but the sample showed the presence of considerable anisotropic material when examined under crossed Nicols. Microscopic tests with acid showed that this impurity was not a carbonate.

The following conditions were found to favour the formation of anisotropic material during the hydration of tricalcium aluminate in steam under pressure:

(1) Moistening the aluminate before autoclaving,
(2) Raising the temperature of the autoclave rapidly,
(3) Using high temperature during hydration,
(4) Using the hexagonal hydrate instead of the anhydrous aluminate for autoclaving.

4. *Stability of the Isometric Hexahydrate*

Attempts were made to produce the anisotropic material in samples of the pure isotropic hexahydrate by autoclaving this substance at high temperatures. The temperatures used were 185°, 200°, 275°, and 300° C. The original hydrate contained 40.02% of water (anhydrous basis) and therefore was of the composition $3CaO \cdot Al_2O_3 \cdot 6.00\ H_2O$. The covered crucibles con-

taining the samples were suspended from the plunger of the bomb. Some alternate condensation and evaporation may have taken place in the crucibles owing to the slight fluctuation of the temperature of the bomb. The results are given in Table I.

TABLE I

HYDROTHERMAL TREATMENT OF $3CaO \cdot Al_2O_3 \cdot 6H_2O$

Temp. of bomb, °C.	Time of treatment, days	H_2O held (dried over CaO)	
		Anhydrous basis, %	Moles
185	18	38.88	5.83
200	13	35.94	5.39
275	6	33.60	5.04
300	5	33.97	5.10

Microscopic examination showed that all the samples contained anisotropic material. This, and the loss of water of hydration in increasing amounts with rising temperature, shows that the hexahydrate is not entirely stable on long treatment under the conditions of the experiments. Fig. 2 shows a typical photomicrograph of a sample treated at 300° C. for five days.

The identification of the anisotropic material in these samples of hydrated tricalcium aluminate, as well as in some of the hydrothermal products described later, presented some difficulty. In the samples treated at 150° to 200° C. it was present mainly as very small crystalline aggregates on the edges of the grains of the hexahydrate, and only an approximate value for the index of refraction could be obtained. The value ($N = 1.58$) was the same as that of the birefringent material in hydrothermal products of the lower-limed aluminates (5), and in appearance the two were similar. There is, therefore, some evidence for assuming that the birefringent material obtained at 150° to 200° C. occurs as hexagonal plates with refractive indices $\omega = 1.576$, $\epsilon = 1.589$ (both ± 0.002). The ordinary tests for free lime were negative. Later it was found that products obtained at 250° C. and above gave a positive White's test for free lime when the test solution was made up with anhydrous materials and the addition of "two drops of water" (to 100 cc. of solution) called for by the usual directions was omitted (10). The anhydrous alcohol–glycerol extraction method (3) also gave a positive result after long refluxing, the initial colour change in the indicator requiring one to four hours, and the total titration as long as 40 hours, of refluxing. Samples treated in the bomb for long periods at 250° C. and above usually contained well formed crystals of calcium hydroxide. An X-ray powder pattern of a sample treated at 275° C. for six days (see Table I) showed distinctly the strongest line of calcium hydroxide, along with a good pattern of the hexahydrate of tricalcium aluminate. Positive tests for lime in the material treated at 150° C. were never obtained, although the anisotropic material seemed to be present in con-

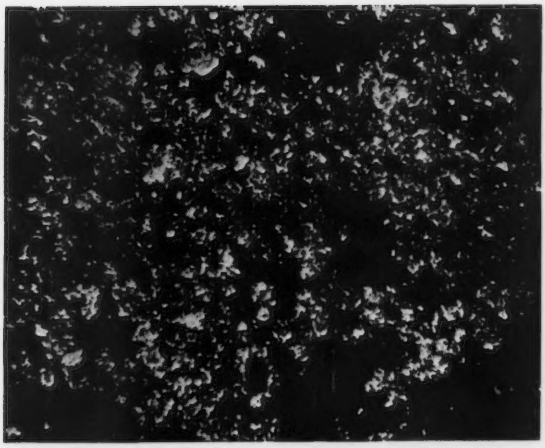

FIG. 1. *Tricalcium aluminate hydrated in saturated steam at 150° C. for four days. Crossed Nicols. Magnification, approximately 450×.*

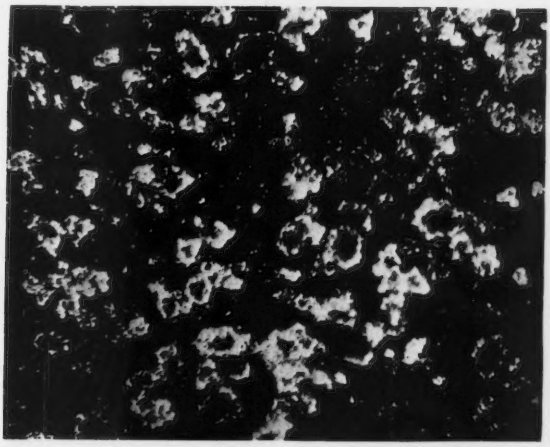

FIG. 2. *Tricalcium aluminate hexahydrate after five days hydrothermal treatment in saturated steam at 300° C. Crossed Nicols. Magnification, approximately 450×.*

siderable quantity. Determinations of free hydrated alumina by the method described in the third paper of this series (5) gave negative results.

5. *Hydrothermal Studies at 150° to 350° C.*

The preliminary results led to a further study of the hydrothermal behaviour of the anhydrous aluminate and its hexagonal and cubic hydrates at 150°, 200°, 300°, and 350° C. In each case the temperature of the autoclave was raised very rapidly to the desired temperature.

Treatments at 150° C. Starting with anhydrous tricalcium aluminate some segregation of anisotropic crystals was observed. On prolonged treatment these gradually disappeared and a sample of the pure isometric hexahydrate was obtained. Starting with the hexagonal hydrate with a water content of from 8 to 13 moles of water, the temporary segregation of anisotropic crystals was much more marked. In 24 hr. the water of hydration for a typical sample dropped to 6.3 moles; in 7 days it was 5.9 moles; and in 14 days it had risen to 6.07 moles. After 14 days' treatment at 150°, the sample had been almost completely changed to the isotropic hexahydrate.

Treatments at 200° C. The results with the hexagonal hydrate were similar to those obtained at 150° C. except that treatment for 14 days gave a molar ratio for water of hydration of 5.6 with a considerable amount of anisotropic matter present. The sample was, however, composed mainly of well formed crystals of the hexahydrate. In one product, White's test for free lime (using the modified test solution) appeared to give a positive result.

Treatments at 250° C. Some hydrolysis of the isometric hexahydrate occurred at this temperature, giving well formed crystals of calcium hydroxide. The greater portion of the original hydrate, however, remained undecomposed. The quantity of water held after 7 to 14 days' treatment varied irregularly between 4.2 and 5.3 moles (28.1 to 35.5% of water, anhydrous basis). When the anhydrous tricalcium aluminate was treated, the results were similar, with somewhat greater variation in the water held (3.2 to 5.5 moles). The anisotropic material predominated in the sample holding 3.2 moles of water, with apparently only a small amount of the hexahydrate. Treatment of the hexagonal hydrate of tricalcium aluminate gave products containing 3.5 to 4.5 moles of water, with large amounts of calcium hydroxide as well as some hexahydrate. In these samples a new crystalline phase was observed for the first time, consisting of transparent, anisotropic, rectangular, prismatic plates with two of the refractive indices close to 1.627.

Treatments at 300° C. Only the hexagonal hydrate was treated at this temperature. The water content of 12 samples after treatment for one to six days varied from 3.2 to 3.8 moles, the average value being 3.6 moles.

Treatments at 350° C. Treatment of the anhydrous aluminate gave products containing hexagonal plates of calcium hydroxide, isotropic spheroids of the hexahydrate, and the rectangular prismatic plates observed in the samples treated at 250° C. The amount of water held varied from 2.8 to 4.8 moles for 7- and 14-day treatments.

Samples of the hexagonal hydrate were treated for periods varying from one hour to 14 days. The water held dropped to less than five moles in one hour and to a minimum of somewhat under three moles in 12 hr. (minimum 18.7% = 2.83 moles of water). After this the amount of water held remained almost constant for some time, but the longer treatments (7, 10, 14 days) gave a higher water content (maximum, 4.1 moles of water). The samples holding least water appeared to be composed almost entirely of calcium hydroxide ($\omega = 1.575 \pm 0.005$, $\epsilon = 1.545 \pm 0.005$), and the transparent, anisotropic, rectangular plates of index 1.627 ± 0.005. In the longer exposures these plates appeared to be partly covered with very small spheroids.

A 3 : 1 molar mixture of calcium oxide and hydrated alumina was wetted with water and treated hydrothermally in the bomb at 350° C. for three days. After the treatment the sample appeared to be composed mainly of crystals of calcium hydroxide and the rectangular prismatic plates.

6. *The Composition of the Hydrothermal Products*

Quantitative determinations of free lime by the anhydrous alcohol-glycerol extraction method were made on a number of the samples treated hydrothermally at the higher temperatures. The extraction of lime from the hydrated mixtures is very slow and the results can be considered only as approximations. A sample of the anisotropic hexagonal hydrate, which, after treatment for seven days at 250° C., showed on microscopic examination calcium hydroxide, the hexahydrate of tricalcium aluminate, and rectangular prismatic plates, gave 20% of free lime (calculated as CaO on the basis of the anhydrous sample). Another sample treated for 12 hr. at 350° C. which appeared to be composed almost entirely of calcium hydroxide and transparent rectangular prismatic plates gave a value of 32.4% calcium oxide. This lime content was higher than that found in any other product. After a 10-day treatment of another sample of the hexagonal hydrate at this temperature, the value obtained was 20% of calcium oxide. The hydrothermal products were entirely soluble in dilute hydrochloric acid at 65° C.; this indicated the absence of free hydrated alumina (5).

The sample of the hexagonal hydrate treated in the bomb for 12 hr. at 350° C., which appeared under the microscope to be almost entirely a mixture of hexagonal plates of calcium hydroxide and rectangular prismatic plates of refractive index 1.627, held 2.96 moles of water per mole of original tricalcium aluminate and contained 32.4% of free lime (calculated as percentage of calcium oxide in anhydrous sample). If the free lime is calculated as calcium hydroxide and it is assumed that the remainder of the lime and water and all the alumina are present in the form of a hydroaluminate, one obtains for this the lime–alumina–water ratio of 1.44 $CaO : Al_2O_3 : 1.25$ H_2O. Presence of any hexahydrate of tricalcium aluminate in the sample would increase the ratio both for lime and water to alumina. The figures for both of these may therefore be considered to be somewhat high. The new hydroaluminate has therefore probably a lime–alumina ratio considerably below 1.5.

Summary and Conclusions

When tricalcium aluminate or its hydrates are treated hydrothermally under conditions favouring hydrolysis, decomposition may occur, with the appearance of birefringent crystals. At the lower temperatures this anisotropic material has a refractive index of approximately 1.58, and below 150° C. prolonged treatment in saturated steam (removal of lime by leaching being excluded) results in recombination to give the isometric hexahydrate of tricalcium aluminate, which is therefore the stable product in this temperature range. As the temperature of the hydrothermal treatment is raised, the permanent segregation of birefringent crystalline phases is favoured, although the main product after prolonged treatment at temperatures below 250° C. is still the hexahydrate. Treatment at temperatures of 250° to 350° C. gives a product containing crystals of a calcium hydroaluminate in the form of rectangular prismatic plates with a lime–alumina ratio of less than 1.5, as well as crystals of calcium hydroxide but no free hydrated alumina. Two of the refractive indices of the crystalline hydroaluminate are close to 1.627.

The low-limed hydroaluminate of refractive index 1.627 is also produced on treatment of a 3 : 1 molar mixture of hydrated lime and hydrated alumina in steam at 350° C. It is therefore a stable product under these conditions.

It thus appears probable that under conditions favouring hydrolysis at least one and possibly two birefringent hydroaluminates may be formed, one at temperatures below approximately 200° C. having a mean refractive index of 1.58 and one at higher temperatures with a refractive index of 1.627.

A greater proportion of the low-limed hydroaluminate of refractive index 1.627 is formed on hydrothermal treatment of the hexagonal hydrate of tricalcium aluminate than when the anhydrous aluminate is used. The autoclaving of the anhydrous aluminate at 350° C. for periods up to 14 days produced a mixture composed mainly of the rectangular plates and calcium hydroxide, although some crystals of the hexahydrate were always present. When the hexagonal hydrate was similarly treated, the product appeared to be composed almost entirely of the rectangular plates and calcium hydroxide and the presence of the hexahydrate was not detected.

The difference in the behaviour of the anhydrous aluminate and its hexagonal hydrate on autoclaving is probably due to the fact that the autoclave must be initially heated and finally cooled through the temperature range in which the hexahydrate of tricalcium aluminate is the most stable product. In this range the anhydrous aluminate is rapidly converted to the cubic hexahydrate, while there is probably no corresponding rapid transformation from the hexagonal to the cubic hydrate. It would appear from the experimental results that when once formed the hexahydrate of tricalcium aluminate is capable of existing at 350° C. in steam approaching saturation and that the hydrolysis of this hydroaluminate, with separation of crystalline calcium hydroxide, possibly occurs only in the presence of the liquid phase.

The experimental data given above are of interest in connection with the steam-curing of precast, Portland cement, concrete products for the purpose of increasing strength or the resistance to the action of sulphate waters. Conditions favouring hydrolysis are probably always present, and if high temperatures are used the birefringent hydroaluminates would be formed as well as the hexahydrate of tricalcium aluminate. The temperature required for the production of the former depends on the form in which the aluminate is present, and would thus probably vary with the age of the concrete at the time of treatment. The inflections in the curves for the change in the tensile and compressive strength of mortar and concrete specimens with the time and temperature of steam-curing described in a previous paper (9) are probably connected with the formation of these hydroaluminates.

Acknowledgments

The authors wish to acknowledge their indebtedness to their colleague, the late Dr. V. A. Vigfusson, for assistance in connection with the microscopic examination of the hydrothermal products and to Dr. M. A. Peacock, of the Department of Mineralogy and Petrography of the University of Toronto, for preparing and interpreting an X-ray powder pattern of one of the hydrothermal products.

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PRELIMINARY EXAMINATION OF SOME TURNER VALLEY CRUDE OILS[1]

By W. G. May[2], K. A. Miners[3], and J. W. T. Spinks[4]

Abstract

Crude oils from eight wells in Turner Valley have been distilled in Stedman columns. Graphs of boiling point vs. volume distilled, refractive index vs. boiling point, and specific refractivity vs. boiling point are presented.

Introduction

In January, 1940, Donald (1) reported details of an investigation of crude oil from Sterling Pacific No. 3 and a few months later Watson and Spinks (5) published data on oil from Foundation No. 1, both wells lying in south Turner Valley. Since that time six more oils from suitable parts of Turner Valley have been investigated in order that the studies might embrace a fair cross-section of the field. The results for the gasoline fraction of the oils are reported here.

Experimental

The experimental procedure was the same as for the oils previously reported (5).

After carrying out a Hempel distillation (see Table I), the crude oil was subjected to a rough fractionation in a steel column, 3 ft. long and 2 in. in diameter, packed with jack chain. The cuts so obtained were closely fractionated in 1 in. diameter Stedman columns. Samples were taken off at intervals of one degree Centigrade or less, and the boiling points corrected to 760 mm. For each sample, n_D^{20} and d_4^{20} were determined and the specific refractivity calculated. Data are recorded graphically in Figs. 1 to 8 (boiling point vs. volume distilled as a percentage of the original crude charge, refractive index vs. boiling point, and specific refractivity vs. boiling point). The data for Royalite 45 do not appear in Figs. 7 and 8, since specific refractivities of oil from this well were not determined. To avoid crowding, data for N. W. Hudson Bay 2 and Royalite 43 oils have been omitted from Figs. 6 to 8 (see (3)). The data for Foundation 1 and Sterling Pacific 3 have been included for the sake of comparison. For tabulated details of samples see References (3) and (4).

Discussion

Fig. 9 is a map of Turner Valley, showing the location of the eight wells investigated. It may be seen that the sampling has covered a wide territory.

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TABLE I

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Volume of charge, 300 ml. Barometer, 720 mm.

Well*	1	2	3	4	5	6
Location	9 of 8	6 of 29	6 of 33	2 of 22	5 of 27	14 of 5
Township–range	18 – 2	18 – 2	20 – 3	20 – 3	20 – 3	19 – 2
Meridian	W-5	W-5	W-5	W-5	W-5	W-5
A.P.I. Gravity, 60° F.	39.0	39.4	40.4	41.1	41.9	44.1
Colour	o, g	o, g	o, g	o, g	o	l, o
First drop, °C.	28	25	–	28	23	22
Temp., ° C.	Volume of cut, %					
Up to 50	1.2	3.6	4.7	4.9	6.7	5.6
50 – 75	2.1	2.7	2.7	3.3	3.0	4.4
75 – 100	5.1	6.2	5.9	6.2	5.7	6.9
100 – 125	7.8	6.8	7.2	7.3	7.2	7.2
125 – 150	7.3	7.0	6.1	6.8	6.8	7.2
150 – 175	6.7	8.0	6.3	6.3	6.4	6.8
175 – 200	6.6	4.4	5.0	5.5	5.5	6.1
200 – 225	5.7	4.8	5.6	6.1	5.3	5.6
225 – 250	7.6	6.8	6.5	5.2	7.0	7.2
250 – 275	7.1	7.3	6.3	7.0	7.0	6.6
Residue	42.0	42.3	42.0	40.0	39.0	35.3
Loss	0.8	0.1	1.7	1.4	0.4	1.1

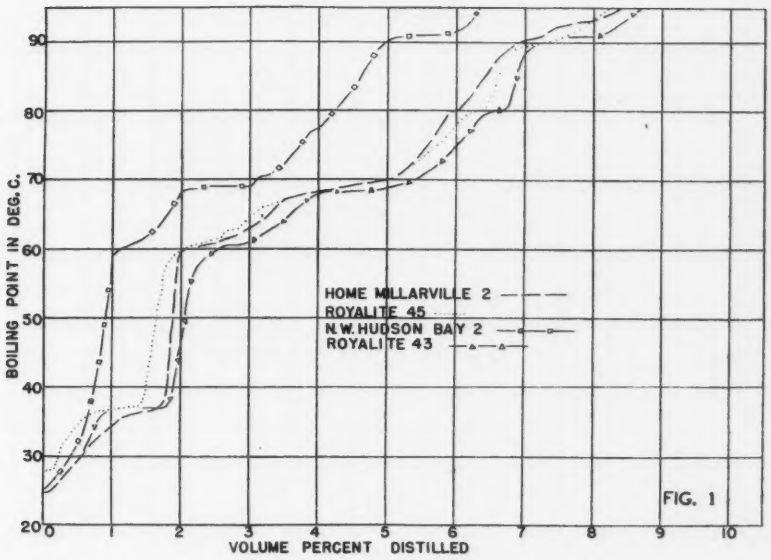
** No. 1, N. W. Hudson Bay 2; No. 2, Royalite 31; No. 3, Home Millarville 2; No. 4, Royalite 43; No. 5, Foothills 6; No. 6, Royalite 45.*

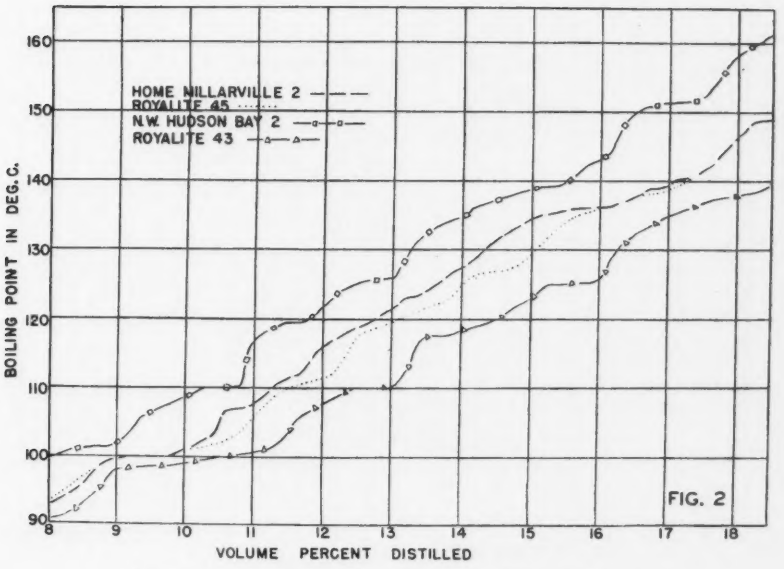
Colour: o, g, orange-green; o, orange; l, o, light orange.

From Figs. 1 to 8 it may be concluded that the same compounds are present in all the oils examined. Any differences in the curves in these figures may be accounted for by differences in degree of fractionation or in the relative amounts of the substances present. Figs. 1 to 4 give some idea of the relative amounts present, and indicate that there are appreciable differences in quantitative composition. Nevertheless, it may be stated that the crudes have essentially similar compositions, indicating a common origin for all of them.

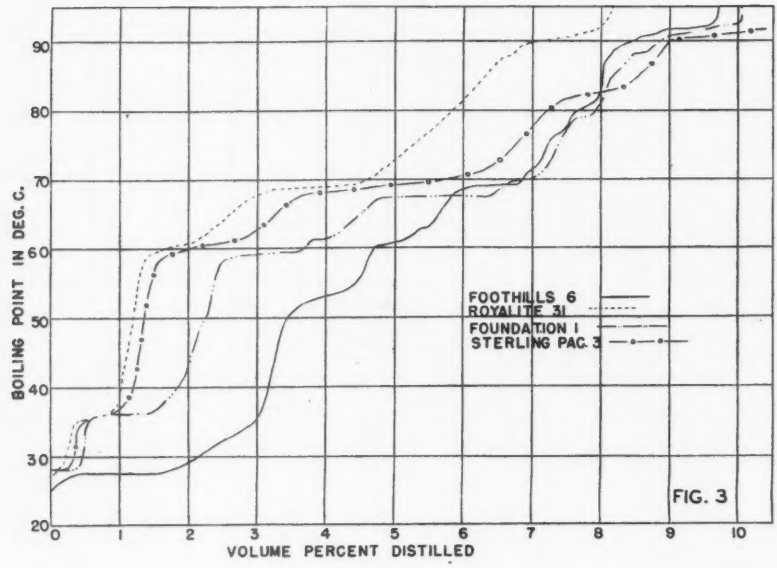
Quantitative estimates of the percentages of some of the compounds present in two of the crudes have already been published (1, 5). After making these quantitative estimates, methods can be developed for the quantitative determination of compounds of special interest, for example, benzene, toluene, and the xylenes (2).

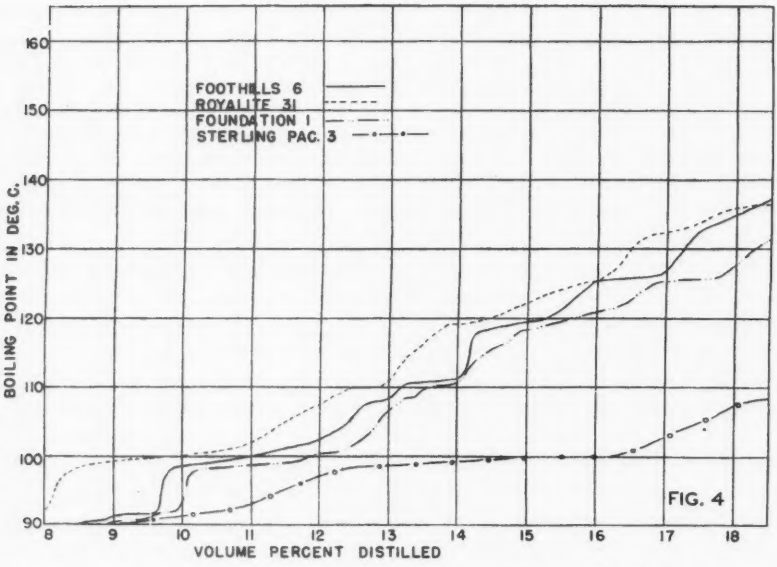
Work of the type summarized in the foregoing is a necessary preliminary step to the isolation of any particular hydrocarbon. The present work indicates that it should be possible by efficient fractionation to produce cuts containing either more than 50% of one particular hydrocarbon or containing only three or four hydrocarbons. From Turner Valley crude, the following hydrocarbons could be so obtained: Isopentane, *n*-pentane, 2-methylpentane,



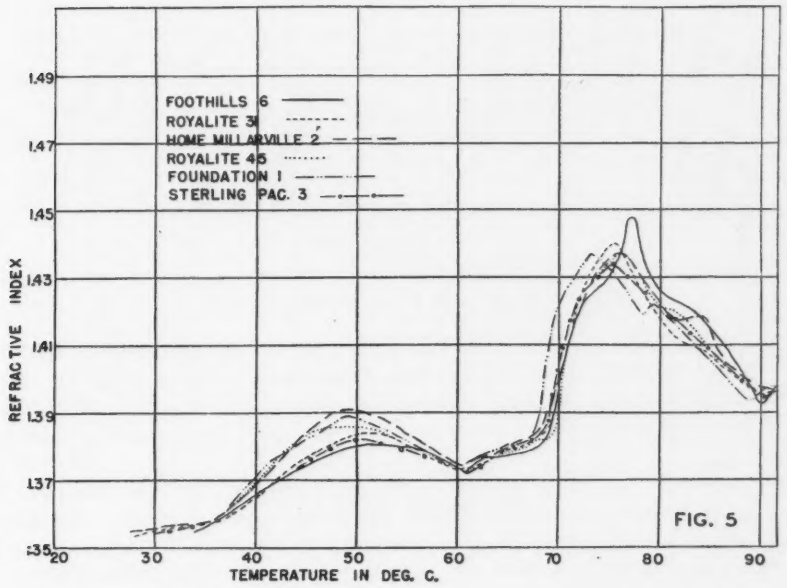


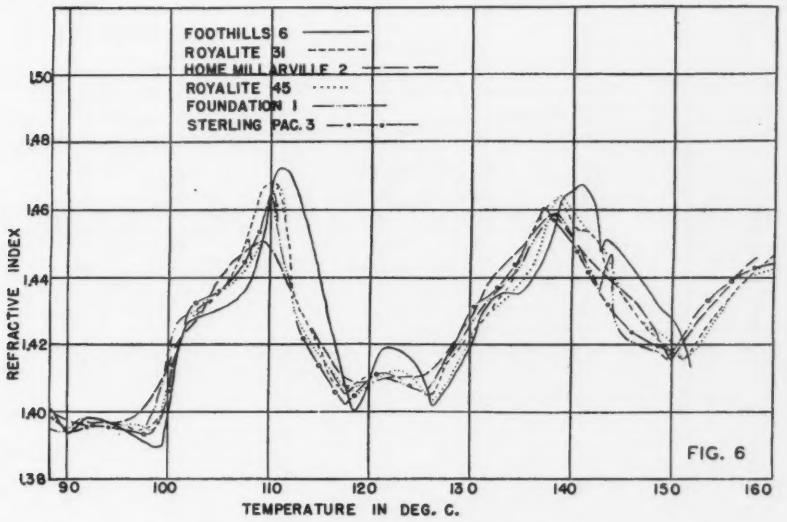
FIGS. 1 AND 2. *Boiling point vs. volume per cent distilled.*



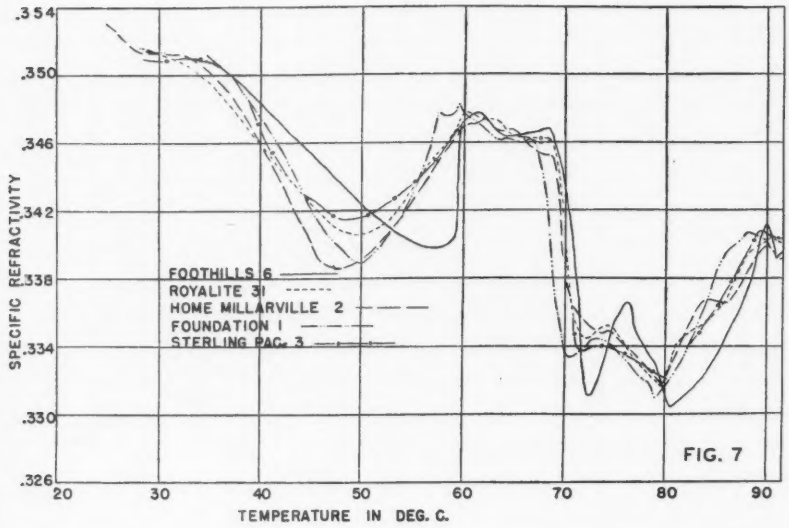


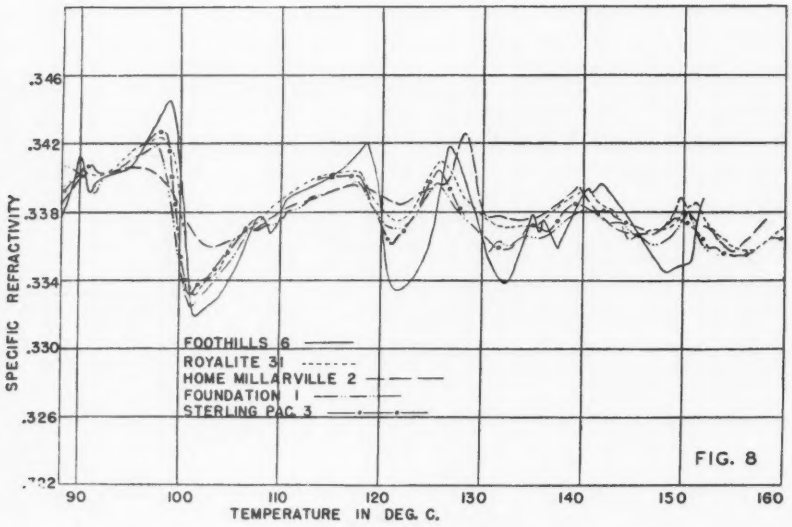
FIGS. 3 AND 4. *Boiling point vs. volume per cent distilled.*





FIGS. 5 AND 6. *Refractive index vs. boiling point for six oils.*





FIGS. 7 AND 8. *Specific refractivity vs. temperature for five oils.*

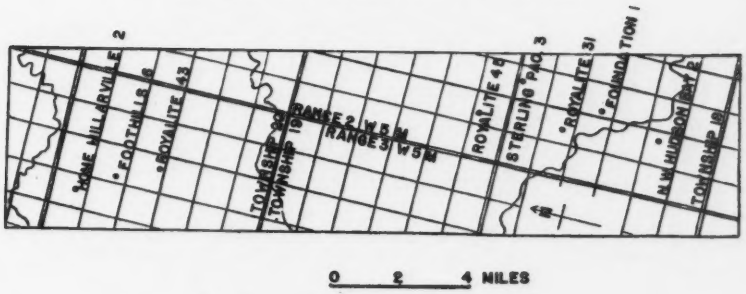


FIG. 9. *Map of Turner Valley oil field.*

n-hexane, methylcyclopentane, cyclohexane, toluene*, branched heptanes*, dimethylcyclopentanes, *n*-heptane*, methylcyclohexane, branched octanes, dimethylcyclohexanes, *n*-octane, ethylbenzene and the xylenes*, and *n*-nonane. Benzene could be separated but would require more than simple fractionation.

To produce pure hydrocarbons, simple distillation would not, in general, be sufficient. However, distillation using a suitable added component, forming azeotropic mixtures with the hydrocarbons to be separated, may be employed to resolve many constant boiling fractions. For other hydrocarbon mixtures, separation may be improved by distillation at reduced pressure.

A further possible use for this type of analysis may be to assist in identifying the geological origin of a particular crude or in mapping out the area covered by a given pool.

Acknowledgments

The Imperial Oil Co. of Calgary kindly donated samples of crude oil. Mr. A. T. Hutcheon and Mr. W. E. Gordon assisted in the distillation of two of the oils.

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* *These hydrocarbons would each constitute 5% or more of the straight run gasoline in the crude (based on results recorded in References (1), (2), and (5)).*

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